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(71) Applicant: BHP MINERALS INTERNATIONAL INC.  
[US/US]; 204 Edison Way, Reno, NV 89502 (US).(71)(72) Applicants and Inventors: DUYVESTYEN, Willem, P.C.  
[US/US]; 2200 Delmonte Lane, Reno, NV 89511 (US).  
HULS, Bernardus, J. [CA/US]; 4496 Interlaken Court, Reno,  
NV 89509 (US). SHRESTHA, Purusotam, L. [US/US]; 3865  
Royer Court, Reno, NV 89509 (US).(74) Agent: KALIL, Eugene, J.; Hopgood, Calimafde, Kalil &  
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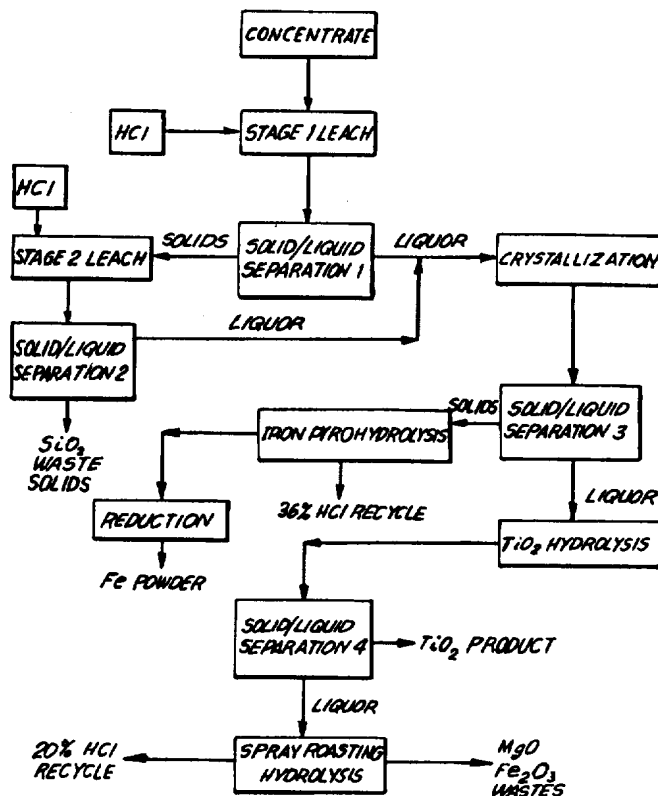
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(54) Title: PROCESSING ILMENITE ORE TO TiO<sub>2</sub> PIGMENT

## (57) Abstract

A hydrometallurgical process is provided for producing pigment-grade TiO<sub>2</sub> from an ilmenite ore concentrate containing by weight a relatively high magnesium content ranging up to about 10 %, an iron content of at least about 15 % and a titanium dioxide content of at least about 25 %. The concentrate is selectively leached with hydrochloric acid at a concentration ranging up to about 30 % of concentrated hydrochloric acid at a temperature ranging from about 25 °C to 80 °C while inhibiting TiO<sub>2</sub> formation by hydrolysis and provide solids containing titanium and a liquid phase. The solids are separated from liquid phase at the aforementioned temperature and the titanium-containing solids leached at a temperature of about 25 °C to 80 °C with hydrochloric acid at a concentration of at least about 18 % and thereby form a pregnant solution of titanium chloride containing iron and magnesium and waste solids containing silica. The waste solids are separated from the solution at a temperature of about 25 °C to 80 °C. The solution is cooled to a low temperature not exceeding about 15 °C sufficient to form crystals of FeCl<sub>2</sub>. The FeCl<sub>2</sub> crystals are then separated from the solution at the stated low temperature, and thereby provide a pregnant solution containing titanium. Titanium-containing solution deficient in iron is subjected to hydrolysis at a temperature in excess of about 75 °C to form a precipitate of TiO<sub>2</sub> and a waste solution containing Mg and Fe chlorides and hydrochloric acid. The TiO<sub>2</sub> precipitate is then separated from the waste solution at a temperature in excess of about 75 °C. The waste solution is then subjected to hydrolysis by spray roasting the solution at a temperature of at least about 600 °C and thereby regenerate HCl and form solids containing MgO and Fe<sub>2</sub>O<sub>3</sub>.



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## PROCESSING ILMENITE ORE TO $\text{TiO}_2$ PIGMENT

This invention relates to the production of pigment grade  $\text{TiO}_2$ .

### STATE OF THE ART

5 Titanium dioxide is considered the principal white pigment of commerce. It has exceptionally high refractive index, negligible color and is quite inert.

There are two main processes for making raw pigmentary titanium dioxide, the sulfate process and the chloride process.

10 The sulfate process was the first used commercially, starting about 1930 in Europe and in the United States. It is a batch process and nearly 60% of all  $\text{TiO}_2$  produced presently is made by the sulfate process.

15 Two forms of titanium ores are available. One is the mineral rutile which is comprised of 95%  $\text{TiO}_2$ . The other is ilmenite. Ilmenite ( $\text{FeOTiO}_2$ ) is plentiful and is the usual source for  $\text{TiO}_2$  pigment. The ore, following grinding, is concentrated by known methods. Concentrated ilmenite ore generally has a  $\text{TiO}_2$  content of at least about 20 40%, and generally in the range of about 45% to 65%  $\text{TiO}_2$ .

25 There are two types of ilmenite; a primary or rock ilmenite and secondary or alluvial ilmenite. The latter has often been upgraded in  $\text{TiO}_2$  content by mother nature, as the  $\text{FeO}$  is leached out. Not all ilmenites are created equal. This is an important finding of the present invention. Some rock ilmenites have part of the  $\text{FeO}$  replaced by  $\text{MgO}$  as the ionic radius  $\text{Fe}^{++}$  is very similar to  $\text{Mg}^{++}$ . In instances where this replacement has occurred, the behavior of ilmenite in an hydrochloric leaching 30 process is different from the ore in which some of the iron has not been replaced by magnesium. Pigment producers have developed several methods for the treatment of ilmenites that do not leach well. One method is to

employ a prereduction step prior to leaching. Another method is to convert the ilmenite into a titania slag which can then be leached.

5 Present day chloride pigment processing methods which utilize a chlorination pretreatment step have their limitations in that they cannot tolerate magnesium levels greater than 1% by weight.

10 Primary ilmenites are not generally amenable economically to produce pigment grade  $\text{TiO}_2$  using conventional technologies. As a consequence, ilmenite deposits containing high magnesium (at least 2%) are difficult to process.

15 The present invention provides a process that can directly convert magnesium-containing ilmenites into pigment, especially those that contain a relatively high amount of magnesium as  $\text{MgO}$ .

20 Thus, an improved hydrochloric acid leaching process is provided which enables the production of pigment-grade  $\text{TiO}_2$  directly from primary grade ilmenite containing relatively high amounts of magnesium.

25 The process depends on the application of a novel combination of operational steps on an intermediate concentrate of ilmenite ore. In producing the concentrate, known beneficiation steps are employed which involve comminution, classification, gravity separation, magnetic separation, electrostatic separation and drying.

#### OBJECTS OF THE INVENTION

30 It is an object of the invention to provide a process for producing pigment-grade  $\text{TiO}_2$  from primary ilmenite.

Another object of the invention is to provide an improved hydrochloric acid leaching process for treating ilmenite ores having a relatively high amount of magnesium.

These and other objects will more clearly appear when taken in conjunction with the following description and the appended drawings.

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### IN THE DRAWINGS

Figs 1 to 3 are flow sheets illustrating the various embodiments of the present invention.

### DETAILS OF THE INVENTION

10 The feedstock employed in carrying out the invention is a high magnesium primary ilmenite. A typical concentrate is that produced by conventional beneficiation processes, the concentrate being finely divided and having an average particle size of less than about 100 microns.

15 A typical concentrate of primary ilmenite is given as follows:

TABLE 1

	Component	Mass %
	TiO <sub>2</sub>	47.6
20	Fe <sub>2</sub> O <sub>3</sub>	14.9
	Cr <sub>2</sub> O <sub>3</sub>	0.17
	V <sub>2</sub> O <sub>5</sub>	0.47
	MnO	0.40
	Nb <sub>2</sub> O <sub>5</sub>	0.08
25	Al <sub>2</sub> O <sub>3</sub>	0.50
	SiO <sub>2</sub>	0.83
	P <sub>2</sub> O <sub>5</sub>	<0.02
	ZrO <sub>2</sub>	0.06
	MgO	3.1
30	CaO	0.37
	S	<0.02
	FeO	32.9

35 As will be noted, the concentrate contains 3.1% of MgO which corresponds to about 1.87% Mg.

Generally speaking, the invention is directed to the treatment of primary ilmenite concentrates containing a relatively high amount of magnesium ranging up to about 40 10% by weight, e.g. 1 to 10% or 2 to 8%, iron in an amount

of at least about 15% and titanium in an amount of at least about 25%.

Referring to Fig. 1, one embodiment of the invention comprises selectively leaching ilmenite concentrate at stage 1 with hydrochloric acid at a concentration ranging up to about 30% of concentrated hydrochloric acid at a temperature ranging from about 25°C to 80°C while inhibiting  $\text{TiO}_2$  formation by hydrolysis and provide solids containing said titanium and a liquid phase. The solids are separated from the liquid phase at said temperature of about 25°C to 80°C. The titanium-containing solids are then leached at a temperature (stage 2) of about 25°C to 80°C with hydrochloric acid of at least about 18% of concentrated HCl and thereby form a pregnant solution of titanium chloride containing iron and magnesium and form waste solids containing silica.

The waste solids are separated (separation step 2) from said solution at said temperature of about 25°C to 80°C. The solution is then cooled to a low temperature not exceeded about 15°C sufficient to form crystals of  $\text{FeCl}_2$  following which the  $\text{FeCl}_2$  crystals are separated (separation step 3) from said solution at the aforementioned low temperature, the  $\text{FeCl}_2$  thereafter pyrohydrolyzed at 600°C to 1000°C to provide a pregnant solution containing titanium.

The titanium-containing solution deficient in iron is subjected to hydrolysis at a temperature in excess of about 75°C to form a precipitate of  $\text{TiO}_2$  and a waste solution containing Mg and Fe chlorides and hydrochloric acid. The  $\text{TiO}_2$  precipitate is separated (separation step 4) from the waste solution at a temperature in excess of about 75°C.

The waste solution is then subjected to pyrohydrolysis by spray roasting said solution at a temperature of at least about 600°C and thereby regenerate

HCl and form solids containing MgO and  $\text{Fe}_2\text{O}_3$ , the acid being thereafter separated from said solids.

The foregoing is illustrated in Table 2 as follows:

TABLE 2

UNIT OPERATION	PURPOSE	TYPICAL CONDITIONS
Stage 1 Leach	Selectively leach titaniferous ore concentrate to solution using low concentration hydrochloric acid, whilst inhibiting $\text{TiO}_2$ formation by hydrolysis	18-24% HCl concentration 25-80°C
Solid Liquid Separation 1	Separate solid and liquid phases at same temperature as Stage 1 Leach	25-80°C
Stage 2 Leach	Selectively leach titaniferous material to solution using high concentration hydrochloric acid	20-36% HCl concentration 25-80°C
Solid Liquid Separation 2	Separate high silica waste solids at same temperature as Stage 2 Leach	25-80°C
Crystallization	Grow crystals of $\text{FeCl}_2$ to permit separation of iron impurities from solution	Controlled cooling to 0-10°C
Solid Liquid Separation 3	Separate $\text{FeCl}_2$ crystals from slurry	Same temperature as Crystallization
Iron Pyrohydrolysis	HCl regeneration and formation of solid ferrous wastes	600°-1000°C
$\text{TiO}_2$ Hydrolysis	Formation of $\text{TiO}_2$ precipitate	90-100°C
Solid Liquid Separation 4	Separation of $\text{TiO}_2$ product	Same temperature as $\text{TiO}_2$ hydrolysis
Spray Roasting pyrohydrolysis	HCl regeneration and formation of solid MgO and $\text{Fe}_2\text{O}_3$ solids <sub>2</sub> product	600°C-1000°

With respect to the unit operations shown in Fig. 2, a summary of the process illustrated is itemized in Table 3 below:

TABLE 3

UNIT OPERATION	PURPOSE	TYPICAL CONDITIONS
Hot Leach 1	Selectively leach titaniferous ore concentrate to solution using hot hydrochloric acid leaching and allow solid $TiO_2$ to form	18-24% HCl concentration 90-110°C
Solid Liquid Separation 1	Separate solid and liquid phases at same temperature as Hot Leach 1	90-110°C
Hot Leach 2	Selectively render iron and magnesium compounds soluble	18-24% HCl concentration 90-110°C
Solid Liquid Separation 2	Separation of $TiO_2$ product	90-110°C
Crystallization	Grow crystals of $FeCl_2$ to permit separation of iron impurities from solution	Controlled cooling to 0-10°C
Solid Liquid Separation 3	Separate $FeCl_2$ crystals from slurry	Same temperature as Crystallization
Iron Pyrohydrolysis	HCl regeneration and formation of solid ferrous wastes	600°-1000°C
Spray Roasting pyrohydrolysis	HCl regeneration and formation of solid $MgO$ and $Fe_2O_3$ solids.	600°C-1000°

As will be noted, a high temperature leach is employed. The  $TiO_2$  product is produced early in the process at separation step 2.

The example illustrated in Fig. 3 of the drawings is summarized in Table 4 as follows:



TABLE 4

UNIT OPERATION	PURPOSE	TYPICAL CONDITIONS
Hot Leach	Selectively leach titaniferous ore concentrate to solution using hot hydrochloric acid and allow solid $TiO_2$ to form	18-24% HCl concentration 90-110°C
Solid Liquid Separation 1	Separate solid and liquid phases at same temperature as Hot Leach 1	90-110°C
Warm Leach	Render all compounds except silica soluble	25-80°C
Solid Liquid Separation 2	Separation of silica impurities	25-80°C
Crystallization	Grow crystals of $FeCl_3$ to permit separation of iron impurities from solution	Controlled cooling to 0-10°C
Solid Liquid Separation 3	Separate $FeCl_2$ crystals from slurry	Same temperature as Crystallization
Iron Pyrohydrolysis	HCl regeneration and formation of solid ferrous wastes	600°C-1000°C
$TiO_2$ Hydrolysis	Form insoluble $TiO_2$	90-110°C
Solid Liquid Separation 4	Separate $TiO_2$ product	90-110°C
Crystallization	Grow crystals of $FeCl_2$ to permit separation of iron impurities from solution	Controlled cooling to 0-10°C
Solid Liquid Separation 5	Separate $FeCl_2$ crystals from slurry	Same temperature as Crystallization
Reduction	Form pig iron and regenerate hydrochloric acid	
Spray Roasting Pyrohydrolysis	HCl regeneration and formation of solid $MgO$ and $Fe_3O_4$ solids	600°C-1000°C

In Table 3, it will be noted that a high temperature leach of 90° to 110°C is employed followed by warm leaching at 25°C to 80°C.

The titanium hydrolysis is carried out at 90°C to 110°C and continued to solid separation step 5.

As will be clearly apparent, the process of the invention is particularly advantageous in the treatment of ilmenite ores containing relatively high amounts of magnesium.

The novel features described hereinabove permit the following:

1. High magnesium primary ilmenite ores, capable of being processed directly to produce  $\text{TiO}_2$  pigment. The processes are also suitable for processing low magnesium primary ilmenite ores.
- 5 2. Primary rock ilmenites capable of being leached with up to 99.5% of the titanium rendered soluble, without the need for preoxidation nor prereduction roasting.
- 10 3. Treatment of titaniferous slags, containing both high and low levels of magnesium and silica wherein  $\text{TiO}_2$  pigment is produced in a similar manner as the treatment for primary ilmenite.
- 15 4. High and variable levels of silicate forming impurities to be tolerated. This is because all iron, magnesium and titanium ionic species are rendered soluble and thus easily separable from insoluble silica. The separation is effected using conventional solid/liquid separation equipment.
- 20 5.  $\text{TiO}_2$  pigment produced from either primary ilmenite or titaniferous slags without constraints on the lower limit of particle size.
- 25 6. Very high purity  $\text{TiO}_2$  pigment produced by means of (optional) repulping with hot/cold acid and hot/cold water. This operation results in an elimination of contamination by magnesium and iron. This can be achieved by the addition of metallic aluminum which selectively reduces  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  while not adversely affecting the
- 30 titanium ion oxidation state.
- 35 7. Crystals of  $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$  which are formed on cooling, thus facilitating good separation from the soluble magnesium compounds and the regeneration of 36%  $\text{HCl}$  to be recycled to the second stage leach.

8. Hydrochloric acid is regenerated and magnesium and iron oxides are recovered by a spray roasting operation on the efflux mixture from the hydrolysis operation.

5        Although the present invention has been described in  
conjunction with preferred embodiments, it is to be  
understood that modifications and variations may be  
resorted to without departing from the spirit and scope of  
the invention as those skilled in the art will readily  
10 understand. Such modifications and variations are  
considered to be within the purview and scope of the  
invention and the appended claims.

## WHAT IS CLAIMED IS:

1. A hydrometallurgical process for producing pigment-grade  $\text{TiO}_2$  from an ilmenite ore concentrate containing by weight a relatively high magnesium content ranging up to about 10%, an iron content of at least about 15% and a titanium dioxide content of at least about 25% which comprises:

selectively leaching said concentrate with hydrochloric acid at a concentration ranging up to about 30% of concentrated hydrochloric acid at a temperature ranging from about 25°C to 80°C while inhibiting  $\text{TiO}_2$  formation by hydrolysis and provide solids containing said titanium and a liquid phase,

separating said solids from said liquid phase at said temperature of about 25°C to 80°C,

leaching said titanium-containing solids at a temperature of about 25°C to 80°C with hydrochloric acid at a concentration of at least about 18% and thereby form a pregnant solution of titanium chloride containing iron and magnesium and waste solids containing silica,

separating said waste solids from said solution at said temperature of about 25°C to 80°C,

cooling said solution to a low temperature not exceeding about 15°C sufficient to form crystals of  $\text{FeCl}_2$ ,

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separating said  $\text{FeCl}_2$  crystals from said solution at said low temperature, and thereby provide a pregnant solution containing said titanium,

5       subjecting said titanium-containing solution deficient in iron to hydrolysis at a temperature in excess of about  $75^\circ\text{C}$  to form a precipitate of  $\text{TiO}_2$  and a waste solution containing Mg and Fe chlorides and hydrochloric acid,

10       separating said  $\text{TiO}_2$  precipitate from said waste solution at said temperature in excess of about  $75^\circ\text{C}$ ,

15       subjecting said waste solution to pyrohydrolysis by spray roasting said solution at a temperature of at least about  $600^\circ\text{C}$  and thereby regenerate HCl and form solids containing MgO and  $\text{Fe}_2\text{O}_3$ .

20       2.   The process of claim 1, wherein said magnesium in the ore ranges from about 2% to 8%.

25       3.   A hydrometallurgical process for producing pigment-grade  $\text{TiO}_2$  from an ilmenite ore concentrate containing by weight a relatively high magnesium content ranging up to about 10%, an iron content of at least about 15% and a titanium dioxide content of at least about 25% which comprises:

30       selectively leaching said concentrate with hot hydrochloric acid at a concentration ranging up to about 25% of concentrated hydrochloric acid at a temperature ranging from about  $90^\circ\text{C}$  to  $110^\circ\text{C}$  and form solids containing said titanium and a liquid phase,

35

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separating said solids from said liquid phase at said temperature of about 90°C to 110°C,

leaching said titanium-containing solids at a temperature of about 90°C to 110°C with hydrochloric acid at a low concentration ranging up to about

25% of concentrated hydrochloric acid and thereby selectively dissolving iron and magnesium and providing solids comprising  $\text{TiO}_2$ ,

separating said  $\text{TiO}_2$  solids from said solution at said temperature of about 90°C to 110°C,

cooling said solution containing iron and magnesium to a low temperature not exceeding about 15°C sufficient to form crystals of  $\text{FeCl}_2$ ,

separating said  $\text{FeCl}_2$  crystals from said solution at said low temperature, and thereby provide a pregnant solution containing said titanium,

subjecting said iron crystals to pyrohydrolysis, thereby regenerating HCl and forming an iron-containing waste solids,

spray roasting said solution of said hydrochloric acid at a temperature of at least about 600°C and thereby further regenerate HCl and form solids containing MgO and  $\text{Fe}_2\text{O}_3$ .

4. The process of claim 3, wherein the magnesium content ranges from about 2% to 8%.

5. A hydrometallurgical process for producing pigment-grade  $\text{TiO}_2$  from an ilmenite ore concentrate containing compounds including by weight a relatively high magnesium content ranging up to about 10%, an iron content of at least about 15% and a titanium dioxide content of at least about 25% which comprises:

selectively leaching said concentrate with hot hydrochloric acid at a concentration ranging up to about 25% of concentrated hydrochloric acid at a temperature of at least about  $85^\circ\text{C}$  with the formation of solids comprising  $\text{TiO}_2$  and a liquid phase,

separating said solids from said liquid phase at said temperature of at least  $85^\circ\text{C}$ ,

warm leaching said titanium-containing solids at a temperature of about  $25^\circ\text{C}$  to  $80^\circ\text{C}$  with a solution of hydrochloric acid of concentration ranging up to about 36% of concentrated  $\text{HCl}$  and thereby solubilizing substantially all of the compounds except for silica impurities,

separating said silica impurities from said solution at said temperature of about  $25^\circ\text{C}$  to  $80^\circ\text{C}$ ,

cooling said solution containing iron and magnesium to a low temperature not exceeding about  $15^\circ\text{C}$  sufficient to produce crystals of  $\text{FeCl}_2$ ,

separating said  $\text{FeCl}_2$  crystals from said solution at said low temperature, and thereby provide a pregnant solution containing said titanium,

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subjecting said  $\text{FeCl}_2$  to pyrohydrolysis, thereby  
regenerating  $\text{HCl}$  and forming a solids product  
containing iron and a pregnant solution  
containing titanium,

5

separating said solids product from said  
solution,

10

subjecting said pregnant solution deficient in  
iron to hydrolysis at a temperature in excess of  
about  $25^\circ\text{C}$  to form a precipitate of  $\text{TiO}_2$  and  
waste solution containing  $\text{Mg}$  and  $\text{Fe}$  chloride and  
hydrochloric acid,

15

separating said  $\text{TiO}_2$  precipitate from said waste  
solution at said temperature in excess of about  
 $25^\circ\text{C}$

20

crystallizing  $\text{FeCl}_2$  from said waste solution,

separating  $\text{FeCl}_2$  crystals from said waste  
solution,

25

and subjecting said waste solution to  
pyrohydrolysis by spray roasting said solution  
at a temperature of at least about  $600^\circ\text{C}$  and  
thereby regenerate  $\text{HCl}$  and form solids  
containing  $\text{MgO}$  and  $\text{Fe}_2\text{O}_3$ .

30

6. The process of claim 5, wherein the magnesium  
content ranges from about 2% to 8%.



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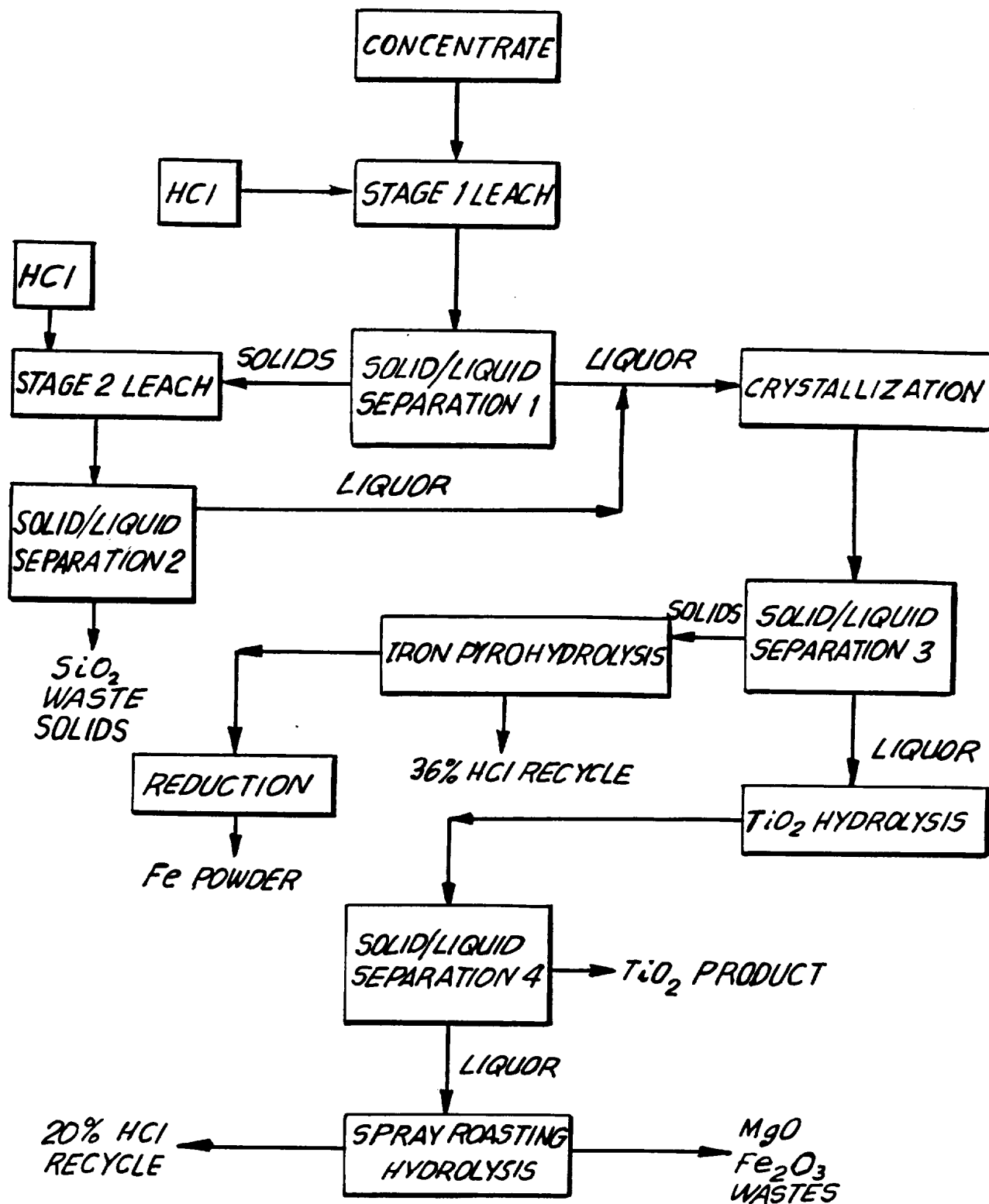


FIG. 1

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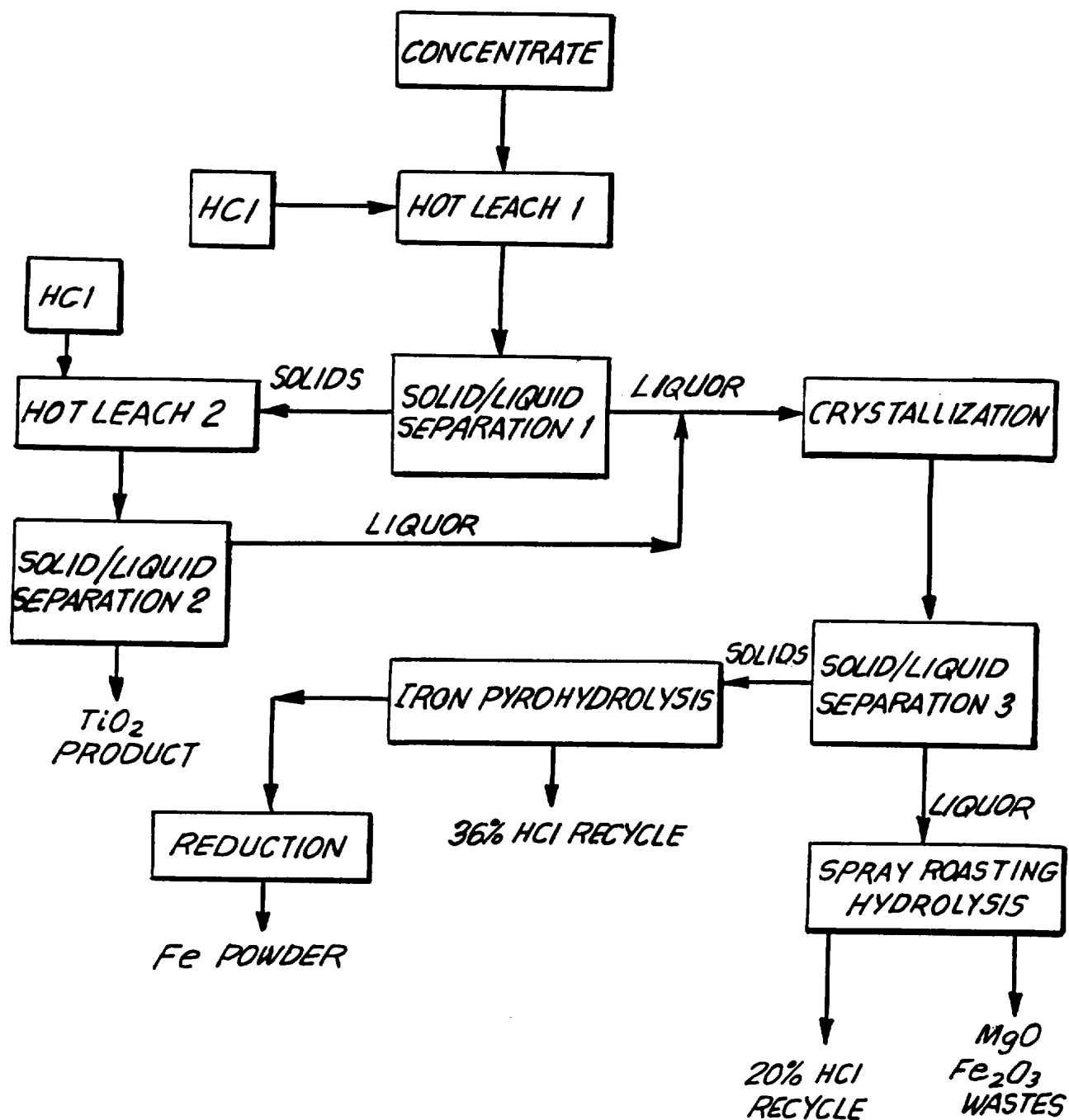


FIG. 2

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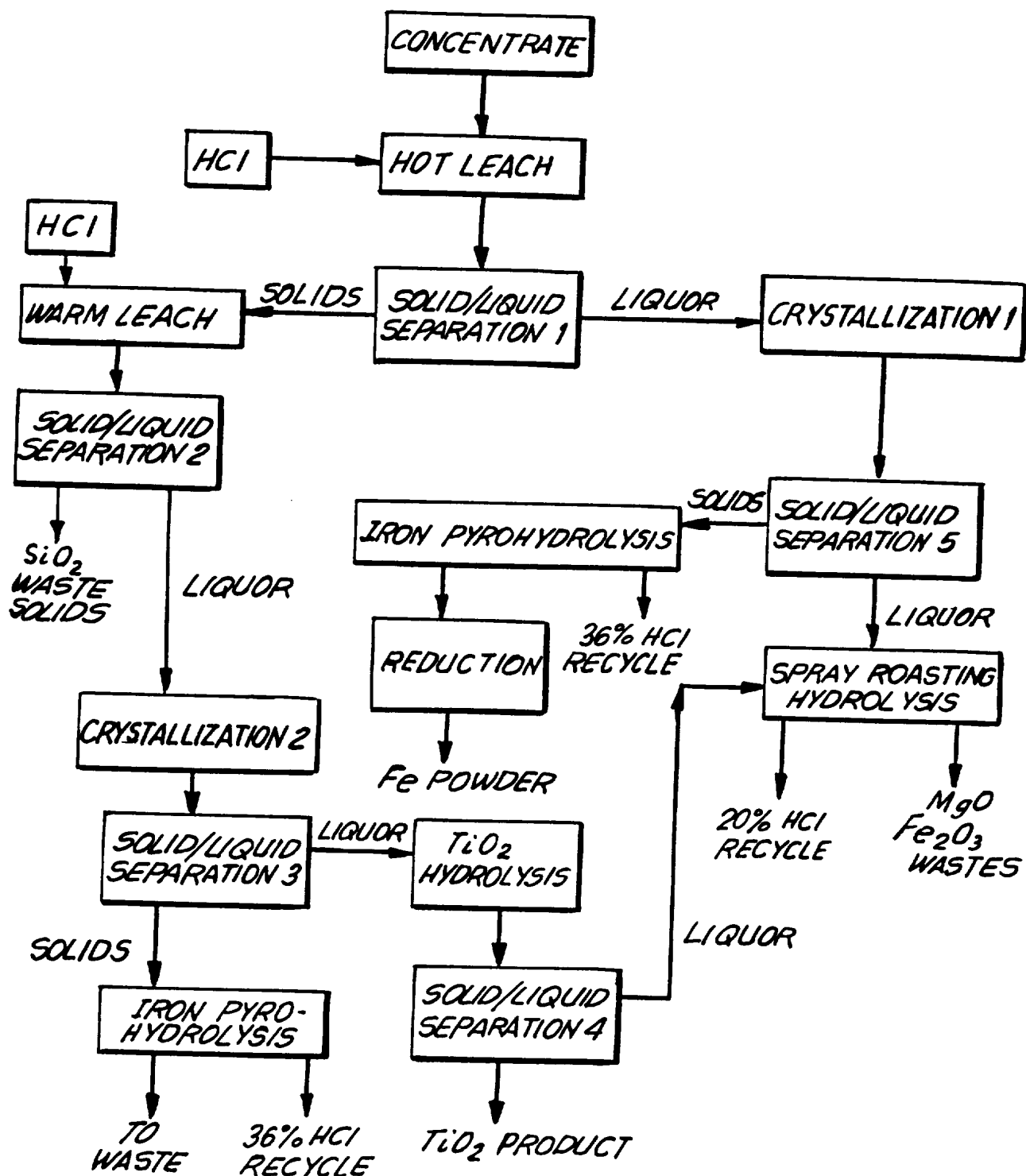


FIG. 3

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/00897

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C01G 23/00; C22B 34/00

US CL : 423/82, 83

According to international Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/82, 83

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
none

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none

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,649,243 (WILLIAMS ET AL) 14 March 1972, col. 2, example 1 and claims 1 and 7-14.	1, 2
Y	US, A, 3,518,054 (KULLING ET AL) 30 June 1970, col. 5, example 1 and the figure.	1-4
Y	US, A, 3,903,239 (BERKOVICH) 02 September 1975, abstract.	1-4
Y	US, A, 4,321,236 (STAMBAUGH ET AL) 23 March 1982, col. 4, claims 1 and 4.	1-4
Y	CA, A, 775,046 (LO ET AL) 02 January 1968, claims 1-3, 5 and 6.	3, 4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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